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STUDY OF THE PROCESS OF FORMATION OF CARBON BLACK PARTICLES DURING DECOMPOSITION OF HYDROCARBONS

V. F. Surovikin and L. S. Kazakov

Study of the process of carbon black formation during the decomposition of hydrocarbons in gases of complete combustion has great significance for the chemical processing of hydrocarbons to obtain highly dispersed carbon black, and also for gas-mazut heating of boilers and industrial furnaces.

Although the process based on the decomposition of hydrocarbon raw material in complete-combustion gases is finding ever broader application in the production of carbon black, it as yet has not been adequately studied. In this process natural gas and air are fed tangentially into a combustion chamber at an excess air coefficient $\alpha = 1.2-1.6$, and the hydrocarbon raw material, atomized by compressed air, is fed axially from the front end of the reactor. Mixing of the flow of raw material and air with complete-combustion gases and the decomposition of hydrocarbons with the formation of carbon black take place in the reaction channel. In this process the intensity of heating and mixing of hydrocarbons with gases is of great significance. Thus, as industrial competence was achieved in the technology of preparing carbon black in reactors with tangential supply of natural gas, it was established at the Novo-Yaroslov, Volgograd, and other factories that carbon black with a specific surface of $70-75 \text{ m}^2/\text{g}$ is obtained stably in this process at a temperature of 1380-1400°C. However, any further increase in temperature does not lead to a noticeable increase in specific

surface, and with a significant rise in temperature the yield of ca. on black drops sharply. This is probably connected with inadequate intensity of the mixing processes.

Solution of the problem of rapid mixing of hydrocarbons with complete-combustion gases is approached in various ways, which in turn is the result of the great number of different designs of reactors. Various methods which are known include twisting the gas flow [1], breaking up the flow of raw material into a number of individual streams [2], contraction of the reaction channel at the point of raw material input [3], and others.

In this article we are concerned with the results of experiments on the process of formation of carbon black in an experimental-industrial reactor under conditions of highly intensive mixing of the hydrocarbon to be decomposed with complete-combustion gases.

Figure 1 shows a schematic diagram of the experimental-industrial reactor*. The reactor consists of a combustion chamber, a nozzle, and the reaction channel. Gas or liquid fuel and air (excess air factor $\alpha = 1.03-1.5$) is fed to the combustion chamber from the front face. The products of complete combustion arrive in the nozzle at a temperature of $1100-1500^{\circ}\text{C}$ and are ejected at a velocity of 350-400 m/s into the reaction channel.

Liquid hydrocarbon raw material is supplied to the nozzle; the hydrocarbon is atomized by the high-temperature gas flow and is mixed with it. The formation of carbon black proceeds in the reaction channel, at the end of which the reaction gas is pulled by water down to a temperature of 700°C.

A preliminary check on a laboratory installation with a raw material consumption of 2.5 kg/hour showed that this method of atomizing the hydrocarbon raw material is highly effective [4, 5]. It was

^{*}The following personnel took part in the experiments: K. F. Berebryakov, A. V. Rogov, and A. I. Pavlov.

possible to obtain carbon black with a specific surface of 70 m²/g from green oil at a temperature of 1280-1300°C, which indicates a high speed of mixing processes and also shows that the process of carbon, black formation occurs in the kinetic region (this last was determined by special experiments) [6].

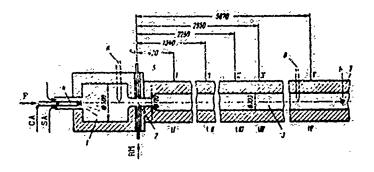


Fig. 1. Schematic diagram of experimental-industrial reactor. F - fuel; CA - compressed air (6 atm); SA - secondary air (0.5 atm); RM - raw material; I-V - sections of the reactor in which samples were taken; I - combustion chamber; 2 - nozzle; 3 + reaction chamber; 4 - pneumatic fuel nozzle; 5 - radial tubes for supply of raw material; 6 - nozzle for supplying water to cool the gases; 7 - insulation and refractory linings; 8 - platinum-platinrhodium thermocouple.

The design of the experimental-industrial reactor retained the linear velocity of the gas in the nozzle, the method of introducing the raw material into the flow, the thermal stress of the combustion chamber volume, and the geometrical shape of the burner, nozzle, and reaction chamber. Since it was established earlier that the formation of carbon black particles and their coagulation and coalescence into chains proceeds in the initial section of the reaction zones, a high gas velocity was designed only for this section of the zone; the velocity was reduced in the remaining portion of the reactor, which made it possible to reduce the length of the reactor. The results, shown in Table 1, indicated good convergence of data obtained from the experimental-industrial reactor with data obtained during work on the laboratory installation [5].

Table 1. Results of technological experiments and calculation of the magnitude of specific surface of carbon black with respect to constants.

, 1	ټ. :	Technological regime of process										Yield	
	Experiment	fuel con- sump- tion, kg/n	raw ca frial flow, ke/h	olion,	raw ma- terial temp.,	temp. in burn- er, oc	pressure in ourrer, H2C	temp. in	pressure in re- action zong, Em 120	ron Y	/pe of material	of carbon black on raw mileri- al, %	-
1	EU-3:1-65 :	170	900	3000	60	1300	34%		1:120		il 40% & ogasol 60%	60.0	1
3	50-32-65 EU-26-65	135 170	680 680	2950 3000	50 . 50	, 1240 1400	306 400		1350 - 1330	The same Mixture oil, 60 thermo	e of green Of, 40%	65,0 42,0	4
5	EU-27-65: EU-12-65	170 136	815 815	3000 3150	80 60	1400 - 1300	400 340		1340 1340	The same Green of therm	0 11 40% & 0Easol 60%	45,3 62,0	,
6 7 8 3	EU-07-65 EU-15-65 EU-03-65 EU-31-65	132 170 137 180	655 655 660 600	3190 3160 3160 3000	60 60 60 60	1300 1360 1350 1450	340 340 340 4 0 0	() 200 0 200	1342 1350 1350 1360		è	49,7 53,8 53,7 35,5	,
۱ ه	.21-1 V -65-	165	640	3000	60	4400	400	0 150	1380		il 40% & ogasol 60%	34,5	
1 1	EU-20-65	152	510	3100	60 1	1260	314	200	1420,	Anthrace 40% & 60%	ns oil green oil	37.8	
2	Novo- Yaroslov carbon black factory	- 60	430	1870	200	, -	(130 -	0. 1000	1490	Green oi thermo	1 50% & gaso1 50%	40,0	٤.
•	Specific surface of carbon black, de termined kinetical A ⁸ X, m ² /6	- 0168	tion nr- k,		stants us		•	Specific surface of carbon black AC determined by theoretical calculation of process by constants r	cific of can black retic exper	of spe- surface ton thec- al versis imental,	Concentration of decomposing hydrocarbon in reaction Sas, woolume	Concentration of carton black particles in reaction gas, no./cm3	
•	1 510	+ 4			1	<u>. </u>		(1-8), 60	1		<u> </u>	<u>.</u>	-
	51,0 2 .58,7 3 86,0	0.	72 :	1,33 • 1013 1,60 • 1013 1,60 • 1013	2,0-10 2:15 · 10 2:15 · 10	1,56		55,3 69,0),977),850-),810	3,50 3,50 2,65	1,14 - 1011 1,54 - 1011 1,44 - 1011	۱
	86,8 5 66,0	0,1 0.3		278 - 1013 278 - 1013	2,25 · 10 2,25 · 10		10-7 10-7	73.0 60,0),842),908	2,60 3,18	1,6 - 1011 1,6 - 1011	
	81.0 82.7 85.0 9 102,0	ŏ,; 0,; 0,; 6,	01 2 82 3	.78 - 1013 .95 - 1013 .95 - 1613 .68 - 1013	2.25 · 10 2.33 · 10 2.33 · 10 2.40 · 10	1:0:	10 ⁻⁷ 10 ⁻⁷ 10 ⁻⁷ 10 ⁻⁸	70,0 78,0 77,5 110,5),834),943),912 ,082	2.57 2.57 2.60 2,33	1,65 - 1011 2,36 - 1011 2,36 - 1011 3,22 - 1011	
1	0 93,0	0.3	75 3	.45 - 1013	2,58 - 10	2.0	10-8	120,0	1	,290	2,49	6,9 - 1011	
1	1 108,0	0.0	04 4	.20 - 1013	2,93 - 10	1,0	10-•	310,0	2	,870	1,98	8,35 - 1011	
1	2 71,0	0,9	98	~	-	-	-	-		-	2,50	_	
_						<u> </u>			<u> </u>		,	·	

The nigh intensity of processes of mixing and heating the raw material leads to a situation in which the rate of carbon-black particle formation approaches the maximum possible rate at the given température. This makes it possible to obtain carbon black with a specific surface of 80-85 m²/g with a yield on the raw material of 42-48% and particles with a specific surface of 100-108 m²/g with a yield of 35-37% on the raw material.

Experiments were conducted with variable concentrations of decomposing hydrocarbons in the reaction gas and with different temperatures in the reaction channel. In the first case the flow of gas from the combustion chamber into the nozzle was maintained constant; while the flow of raw material was varied from 450 to 900 kg/hour. In the second case the flow of raw material was held constant at 600-650 kg/hour while the temperature in the reaction channel was varied by regulation of the excess air coefficient in the burner. The experimental results are shown on Figs. 2 and 3 and, partially, in Table 1. An increase in the supply of hydrocarbon raw material to the nozzle leads to a reduction in temperature in the reaction channel from 1450 to 1320°C, and also to a drop in the specific surface of the carbon black from 120 to 52 m²/g. With variation of the temperature in the reaction channel while the flow of raw material is maintained constant, the change in specific surface of carbon black with temperature is considerably less sharp. A growth in specific sarface of the carbon black from 85 to 100 m²/g is observed when the temperature is changed from 1380 to 1425°C.

Thus, in the first case the average change in specific surface with temperature comprises 0.62 m²/g per °C, while in the second case it was 0.23 m²/g per °C. Data from the experiments indicate that the magnitude of specific surface of carbon black in the furnace process is determined by two basic factors: temperature and the concentration of hydrocarbon raw material in the reaction zone.

Experiments were conducted to study the transformation of hydrocarbons with the formation of carbon black along the length of the reaction channel according to a procedure developed earlier [4]. For

this purpose watercooled gas samplers were installed in various sections of the reaction channel, as shown on Fig. 1. The samples of carbon black and gas which were drawn off were analyzed by known methods. The yield, specific surface, and oil absorption of the carbon black and the composition of the gas were determined at each sampling point; the VTI-2 gas analyzer was used. The concentration of water vapor in the reaction gas was determined by calculation from the hydrogen and oxygen balance.

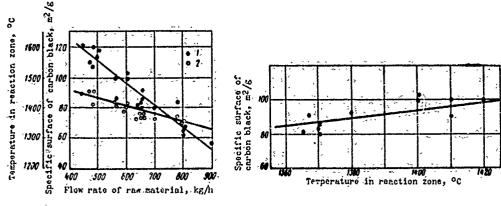


Fig. 2 Fig. 3

Fig. 2. Dependence of specific surface of carbon black and process temperature on flow rate of hydrocarbon. 1 - specific surface of carbon black; - pr cess temperature.

Fig. 3. Temperature dependence of specific surface at a constant hydrocarbon flow rate.

In several sections samples of carbon black were taken at the wall of the reaction chamber and also along its axis. The specific surface of carbon black drawn from the different points was identical. The degree to which hydrocarbon decomposition was completed was evaluated according to the optical density of a benzene extract of the carbon black.

The temperature of gases in different sections was determined by thermochemical calculation based on the composition of the gas, with consideration of heat losses into the ambient medium. In some sections, temperature measurements were made with a platinum-platinrhodium thermocouple and with a radiation pyrometer. The nature of the change in temperature and in gas composition along the length of the reaction

zone is shown on Figs. 4 and 5. Direct measurement was not possible in the zone of maximum temperature, owing to the instantaneous destruction of the thermocouple. The results of the experiments are shown in Table 2.

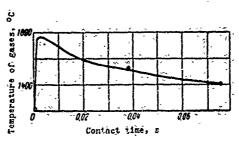


Fig. 4. Calculated curve of the temperature change along the length of the reaction channel.

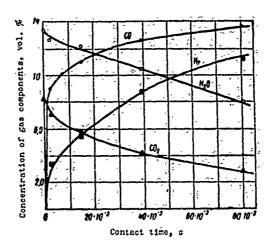


Fig. 5. Kinetics of gas formation during decomposition of green oil in the reaction zone. \triangle - carbon dioxide; \bullet - carbon monoxide; \blacksquare -hydrogen; 0 - water vapor.

Sampling of carbon black along the length of the reaction channel showed that the process of formation and growth of carbon black particles is completed in the industrial reactor with a contact time of $2.4 \cdot 10^{-3}$ s. The specific surface of the carbon black is identical in the initial and final sections of the reaction zone.

Table 2. Kinetics of carbon black formation and of the change in the gas composition in the reaction zone of the industrial reactor.

Experiment	Consumption of diezel fuel, kg/h	Air flow,	Temp. in burner *G	Consumption of raw zn- , terial (Green oil), KE/h	Temp. at end of re- action zone,	Contact time,	Specific surface of carbon black, m ² /g		Crtical density of benzene extraction ine pro- scale	
EU-01-60	130	2450	1250	400	1380	2,4 - 10-5	103,6	0,86	_	1
						15,5 - 10:3	0,101	-0,86		2
· ·	Ĵ.					38,4 - 10-3	103,6	0.80	_ ,	3
		1				6,08	100.0	0,89		4
EU-03-66	155	2500	1259	400 -	1380	2,4 - 10-3	113.5	0,86	0,05	5
•				٠,]	15.5 - 10-3	114,0	0,89	0.03	6
· .		1	ļ	5]	38.4 - 10-3	105,5	0,83	0.02	7
		·]	1		}	0,08	100,5	0.84	10,0	e
EU-04-06 .	90	2500	1270	410	1390	2.4 - 10-3	102,0	0,82	0,00	9.
					1-	15,5 - 10-3	107.0	0.90	0.02	i o
	1		ł			38.4 - 10-3	90,0	0.82	0.01	11
٠		1	Į	ł		0,08	105,0	0.84	0.01	12

$\cdot \mid$		Compositi	on of re	action gas	s, vol. %	Temp. of	Value of PCO.PH.	Equilibrium constant of water gas [13, 14, 15]:	Concen- tration	
-	co.	CO.	CII.	11,	H ₁ 0	Ŋ,	reaction gas, °C	PCOPII:0	Ke PCOFNIO	E\m3 tu Eas. plack carpon
Ī	7,06	9,15	0,2	3,49	12,70	67,60	1862	0,212	0,212	36,4
2	5,90	11,00	0,2	5,64	12,10	64.46	1620	0,249	0,242	38,8
3	4,25	12,60	0,1	8,77	10,50	63 88	1500	0,285	0,268	40,0
4	2,92	13,50	0.1	-11,10	8,15	64.23	1380	0,310	0.319	39,0
5	7,27	11,50	0,4	4.03	-12,10	65,10	1800	0.210	0.206	32,2
6	5,87.	13,20	0,4	5,52	11,00	64,01	1680	0 223	0,229	41,0
7	5,22	14,15	0.4	7.92	10,50	61,81	1500.	0,278	0,268	42,8
8	4,90	14,80	0,2	9,09	9,07	61,94	1380	0,311	0.310	41,2
9	5.80	13,60	0,1	5.6	12.42	62,68	1900	0,192	0,189	33,4
10	5,42	14,55	0,2	7,43	10,65	61,95	1760	0.258	0.213	32,0
1 1	5,07	15,00	0,0	8,25	9,43	62,25	1540	0,296	0,277	31,4
1 2	4,54	17,20	0,0	9,82	8,43	61,01	1390	0,308	0,304	36,0

The magnitude of optical density of a benzene extract of carbon black shows a negligible concentration of hydrocarbons on the carbon black, i.e., at a contact time of $2.4 \cdot 10^{-3}$ s complete decomposition of hydrocarbons takesplace. Since processes of diffusion and heat transfer can also take place in this time, it is evident that the time of the actual process of formation and growth of carbon black particles is significantly less than the measured time.

The postact time in the reaction zone of industrial reactors should be increased to 0.05-0.07 s and more, depending on the type of carbon black to be produced; in this way the optical density of the benzene extract is held within the limits 0.005-0.01, according to the requirements of the user. The process of formation and growth of carbon black particles occupies no more than 1-2% of the total contact time in the reaction zone of an industrial reactor.

Apparently, under the considered conditions evaporation of a drop of hydrocarbon raw material precedes the formation of carbon black particles. The obtained experimental results contradict the procedure for calculating reaction zone length which was proposed in work [10], where the stage of evaporation of drops of raw material is taken as the base. Thus, with a contact time of 2.4·10⁻³ s there are no drops of raw material in the reaction zone, and only the optical density of the benzene extract of the carbon black permits detecting a small quantity of undecomposed hydrocarbon on the surface of carbon black particles.

The experiments showed that in industrial reactors the formation of carbon black during decomposition of raw materials proceeds at a higher temperature than that which is usually measured at the end of the reaction zone. A rapid growth in temperature is observed in the initial period. However, there is no foundation for connecting the rise in the rate of carbon black particle formation with a certain growth in temperature and the achievement of a maximum, since special experiments using individual hydrocarbons [6] having a large induction period showed that, despite the completion of oxidation processes long before the moment of carbon black formation, the character of the kinetic curves of particle formation rate is identical in all cases.

The obtained experimental data were used in an effort to calculate the process of formation of carbon black particles with a definite specific surface of the carbon black at the output of the reactor according to the given parameters of the technological process. The essence of the proposed calculation method is as follows. Given flow rates of fuel, air, and raw material, and also given temperature in

the reaction zone and composition of reaction gases are used to determine the total volume of reaction gas v^2 . The concentration in the reaction gas of carbon formed as carbon black particles is determined from the following equation:

$$C^{\epsilon} = \frac{G\eta}{V10\delta}, \tag{1}$$

where C^c is the concentration of carbon in the reaction gas in g/cm^3 ; C is the flow rate of raw material, kg/h; n is the yield of carbon black in %; V is the volume of reaction gas, m^3/h .

In order to determine the concentration of carbon black particles in the reaction gas, it is possible to apply the equation developed by N. N. Semenov [8] for branched chain processes with quadratic breaks in the chain:

$$n = \frac{2n_0 \left(e^{\sqrt{q}t} - 1\right)}{\sqrt{q} + (f - g) + \left(\sqrt{q} - (f - g)\right) e^{\sqrt{q}t}};$$

$$\sqrt{q} = \sqrt{(f - g)^2 + 4g_0 n_0},$$
(2)

where n is the concentration of carbon black particles at moment of time t, no./cm 3 ; n_0 , (f - g), and g_0 are constants of equation (2); t is the time of contact of the hydrocarbon in the reaction zone in seconds.

At large t, formula (2) is simplified and takes the form

$$n = \frac{2n_0}{1/(I-R)^2 + Ag_0n_0 - (I-R)}.$$
 (3)

The specific surface of the carbon black was determined at the moment of exit of reaction products from the reaction zone. Therefore it is considered that the final concentration of carbon black particles which was found according to equation (2) at t = 0.07 s is equal to the time of contact of the hydrocarbon in the reactor.

For the calculations we used the constants n_0 , (f - g), and g_0 , determined earlier [6, 9] on a laboratory installation for green oil. Interpolated values of these constants were used only within the

investigated temperature interval of 1315-1360°C. An attempt to extrapolate the values of these constants to the temperature interval 1360-1240 [sic] °C did not yield satisfactory results.

Knowing the concentration of carbon in the reaction gas (C^0) and the number of particles (n), we will determine the weight of an average particle g_{nv} in grams:

$$\varepsilon_{av} = \frac{c^c}{n}$$

and the volume of an average particle:

$$V_{av} = \frac{E_{av}}{\rho}$$

where ρ is the true density of a carbon black particle (we take $\rho = 1.87 \text{ g/cm}^3$).

The average diameter of carbon black particles and the specific surface are determined according to known formulas:

$$v_{av} = \sqrt{\frac{6}{\pi}} \frac{V_{av}}{V_{av}} c.v.$$

$$A = \frac{60000}{V_{av}}, a' / 2$$

where d_{av} A is the average diameter of a particle in 3 .

The results of calculations by this procedure are shown in Table 1. The calculation demonstrates that the maximum divergence of values of specific surface for carbon black obtained experimentally and determined by calculation does not exceed 20%. The application of the constants obtained in laboratory conditions to calculate the industrial process in conditions of different concentrations (by the Semenov equations) gives good agreement with experimental data in terms of the specific surface of the carbon black. This indicates that the process of formation of carbon black particles in the industrial reactor is described well by the Semenov equations for a branched process with quadratic breaks in the chain, and that these equations can be used with an adequate level of accuracy for calculating industrial process for manufacturing carbon black.

In the experiments it was noticed that the concentration of particles in the reaction gas does not depend on the concentration of decomposing hydrocarbon. At a constant temperature, an increase in hydrocarbon concentration leads only to an increase in the size of the formed particles. An analogous phenomenon was observed in experiments with a benzene-nitrogen mixture [7], and also in experiments on the decomposition of toluene in complete-combustion gases. In experiments with benzene the growth in particle yield ended at a benzene concentration of 1.3%, while in experiments with toluene the value was 1.)%. It is possible to assume that during the decomposition of highly aromatized hydrocarbons the cessation of particle growth sets in also al a concentration no higher than 1.9%. In connection with this, a change in the concentration of hydrocarbon in an industrial reactor, which comprises, as a rule, no less than 2.5%, will not affect the yield of particles in a unit of reaction volume, but will only lead to a change in the sizes of the growing particles. This is explained by the concurrent nature of the processes of particle formation and growth and also by the acceleration of the process of seizure of new radicalnuclei by the rapidly increasing surface of forming and growing particles.

Study of the change in reaction gas composition with time shows that over the course of the process there is interaction of water vapor and CO₂ with the dispersed carbon which is being formed. A growth in the concentrations of hydrogen and carbon monoxide is observed. Calculation shows (see Table 2) that the components of the reaction of water gas are found in equilibrium in any segment of time. This result corresponds to assumptions expressed earlier [12].

Conclusions

The process of formation of carbon black particles in an industrial reactor can be described by the equation of N. N. Semenov for branched chain processes with quadratic breaks in the chain. The specific surface of the carbon black can be determined by theoretical calculation according to the technological parameters of its manufacture.

The heatup and evaporation of hydrocarbon raw material, and also the formation and growth of carbon black particles, occupy about $(2-3)\cdot 10^{-3}$ s in an industrial reactor with gases moving at a speed on the order of 300-400 m/s in the zone in which they are mixed with the hydrocarbons.

Atomization of the hydrocarbon raw material by high-temperature gases from the complete combustion of the fuel at a high relative rate of motion ensures that the raw material will be heated at a high rate. In this process the magnitude of specific surface of the carbon black depends on temperature and on the concentration of hydrocarbons in the reaction gas.

The temperature of the gases in the reaction channel of an industrial reactor is not constant along its length. This temperature grows rapidly in the initial zone, due to the flowing of exothermic reactions; it achieves the maximum at the moment of total consumption of oxygen and then is reduced due to exothermic reactions of gasification and to heat losses into the environment.

The composition of water gas varies over the length of the reaction zone, but at any moment of time the water gas reaction is in equilibrium, corresponding to the temperature of the reaction products.

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DATA HANDLING PAGE 39-TOPIC TAGS OFACCESSION NO. 98-DOCUMENT LOC. TT0000122 hydrocarbon separation, hydrocarbon combustion, gas velocity, gas flow, temperature measurement, thermo-OS-TITLE STUDY OF THE PROCESS OF FORMATION OF CARBON BLACK PARTICLES DURING chemical property, optic density, particle production DECOMPOSITION OF HYDRO-CARBONS -U-07, 20 42 AUTHOR CO-AUTHORS 10-DATE OF INFO SUROVIKIN, V. F. ;16-KAZAKOV, L. S. -:----67: 68-DOCUMENT NO. 43-SOURCE GAZOVAYA PROMYSHLENNOST! FTD HT-23-330-69 (RUSSIAN) 69-PROJECT NO 72301-78 63-SECURITY AND DOWNGRADING INFORMATION 64-CONTROL MARKINGS 97-HEADER CLASH UNCL UNCL. O NONE 76-REEL/FRAME NO. 77-SUPERSEDES 78-CHANGES 40-GEOGRAPHICAL AREA NO. OF PAGES UR 1891 0573 CONTRACT NO. X REF ACC. NO. PUBLISHING DATE TYPE PRODUCT REVISION FREQ 65-BC8018177 TRANSLATION. NOŃE 02-UR/0000/67/012/008/0040/0046

ABSTRACT

(U) The process of formation of carbon black particles in an industrial reactor can be described by the equation of N. N. Semenov for branched chain processes with quadratic breaks in the chain. The specific surface of the carbon black can be determined by theoretical calculation according to the technological parameters of its manufacture. The heatup and evaporation of hydrocarbon raw material, and also the formation and growth of carbon black particles, occupy about (2-3) times 40 (minus superscript 3)s in an industrial reactor with gases moving at a speed on the order of 300-400 m/s in the zone in which they are mixed with the hydrocarbons. Atomization of the hydrocarbon raw material by high-temperature gases from the complete combustion of the fuel at a high relative rate of motion ensures that the raw material will be heated at a high rate. In this process the magnitude of specific surface of the carbon black depends on temperature and on the concentration of hydrocarbons in the reaction gas. The temperature of the gases in the reaction channel of an industrial reactor is not constant along its length. This temperature grows rapidly in the initial zone, due to the flowing of exothermic reactions; it achieves the maximum at the moment of total consumation of oxygen and then is reduced due to exothermic reactions.